e^-

Electron collision driven chemistry

Jonathan Tennyson

University College London

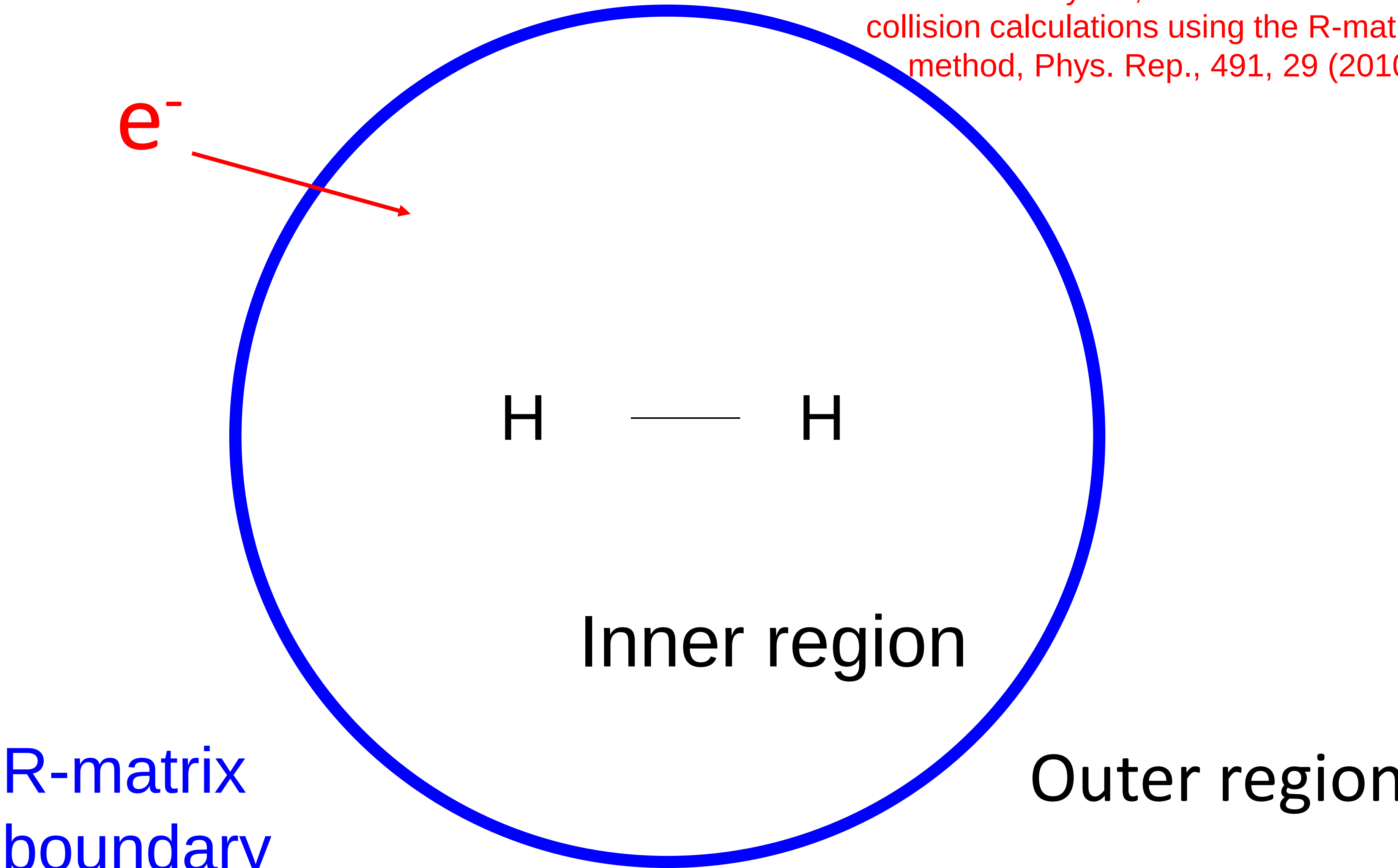
Outer region

Inner region

KIDA workshop
Paris, May 2015

The R-matrix method

J. Tennyson, Electron - molecule collision calculations using the R-matrix method, Phys. Rep., 491, 29 (2010).



Elastic scattering

AB + e ⟶ AB + e

Electronic excitation

What is the electron energy distribution function (EEDF) ?

AB(v”=0) + e ⟶ AB(v’) + e

Rotational excitation

AB(N”) + e ⟶ AB(N’) + e

Dissociative attachment / Dissociative recombination

AB + e ⟶ A^- + B

⟶ A + B^-

Impact dissociation

AB + e ⟶ A + B + e

Impact ionization (e,2e)

AB + e ⟶ AB + e + e

Processes: at very? low impact energies

Process	Reaction	Relevance
Elastic scattering	AB + e → AB + e	Irrelevant
Electronic excitation	AB + e → AB* + e	Ionospheres
Vibrational excitation	AB(v”=0) + e → AB(v’) + e	Planetary atmospheres
Rotational excitation	AB(N”) + e → AB(N’) + e	ISM / PDR
Dissociative attachment / Dissociative recombination	AB + e → A^- + B → A + B^-	ISM
Impact dissociation	AB + e → A + B + e	Irrelevant?
Impact ionization (e,2e)	AB + e → AB + e + e	irrelevant?

Processes: at low impact energies

All go via $(AB^{-})^{**}$. Can also look for bound states

Also consider:

Photoionisation

$$AB + h\nu \longrightarrow AB^{+} + e$$

www.quantemol.com

Rotational excitation of molecular ions: Astrophysical importance

Photon dominated regions (PDRs)
Electron density, $n_e \sim 10^{-4}\ n(H_2)$
Rotational excitation cross section
$\sigma_{electron} > 10^5\ \sigma_{molecule}$
Radiative lifetime < mean time between collisions

Therefore:
Observed emissions proportional to
$\sigma_{electron}$ x column density

Similar arguments hold for vibrational excitation

Rotational excitation of molecular ions: Theoretical models

Standard model

Dipole Coulomb-Born approximation

Only considers (long-range) dipole interactions

Eg for H_3^+ this gives very small excitation rates

No experimental data available for electron impact rotational excitation of molecular ions

Rotational excitation of molecular ions: Theoretical models

Standard model
Dipole Coulomb-Born approximation
Only considers (long-range) dipole interactions

Eg for H_3^+ this gives very small excitation rates

(Almost) No experimental data available for electron impact rotational excitation of molecular ions

D. Shafir, S. Novotny, H. Buhr, S. Altevogt, A. Faure, M. Grieser, A. Harvey, O. Heber, J. Hoffmann, H. Kreckel, L. Lammich, I. Nevo, H.B. Pedersen, H. Rubinstein, I.F. Schneider, D. Schwalm, J. Tennyson, A. Wolf & D. Zajfman,
Rotational cooling of HD^+ molecular ions by superelastic collisions with electrons,
Phys. Rev. Lett., 102, 223202 (2009)

Results of several detailed studies

$\Delta J = 1$

$\mu > \mu_c$ Coulomb-Born model satisfactory

$\mu < \mu_c$ Short range interactions important

Find $\mu_c \sim 2$ Debye

$\Delta J = 2$

Dominated by short range interactions

Always important, can be bigger than $\Delta J = 1$

$\Delta J > 2$

Determined by short-range interactions

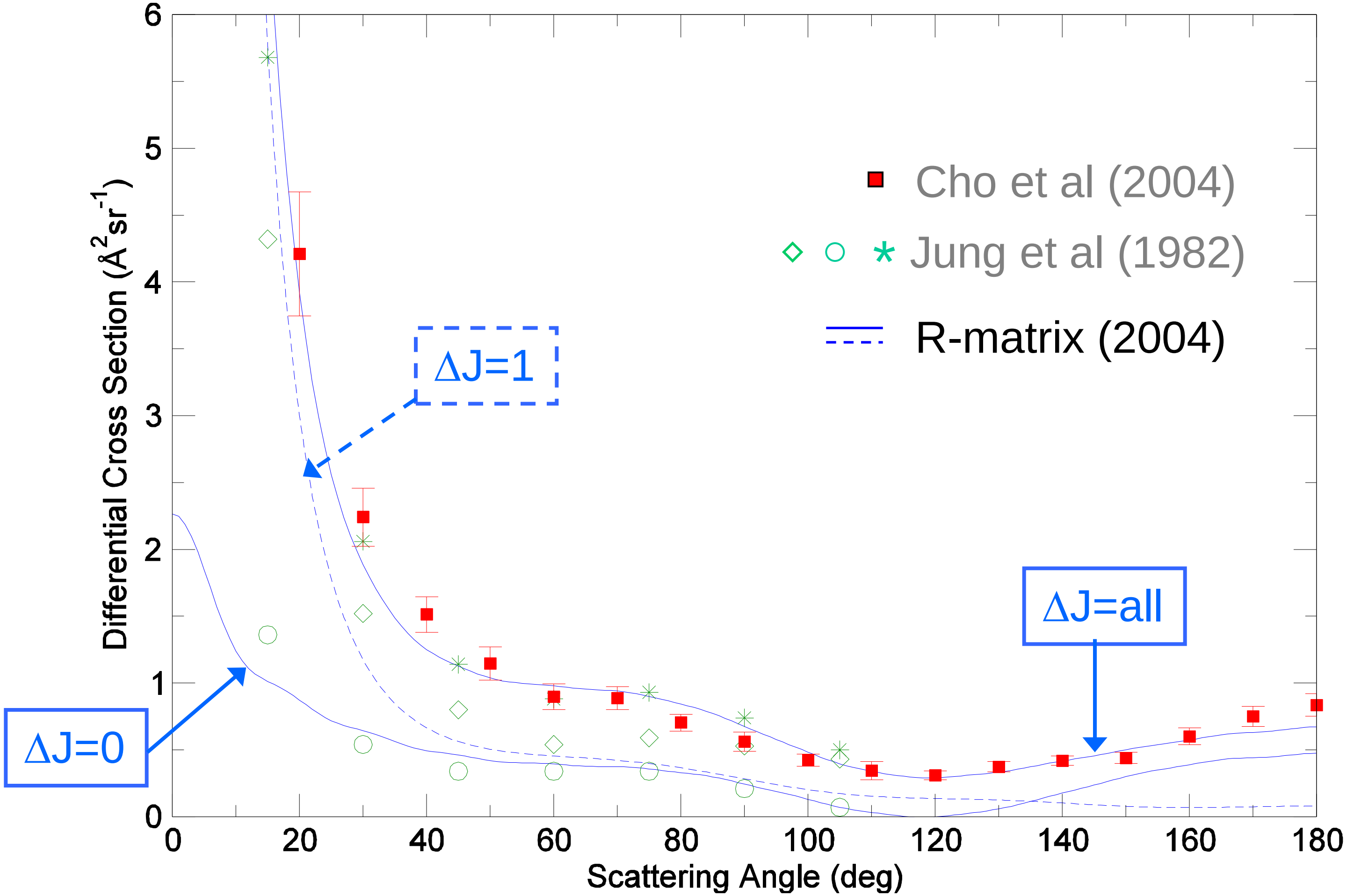
Usually small, but $\Delta J = 3$ can be significant

For light molecules (H containing),

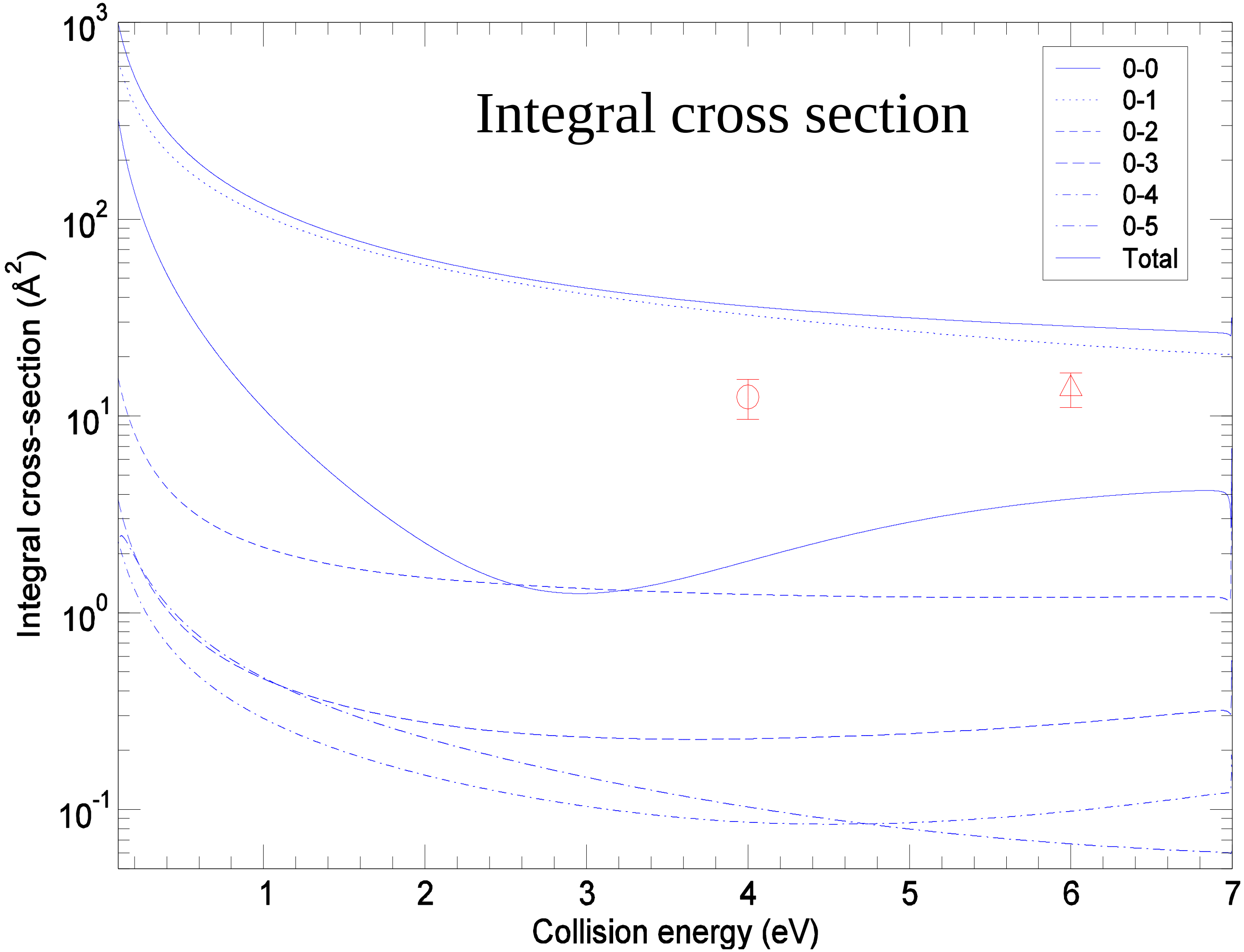
simple cross-sections modification near threshold

Electron – water rotationally resolved cross sections:

Differential cross sections (DCS) at 6 eV

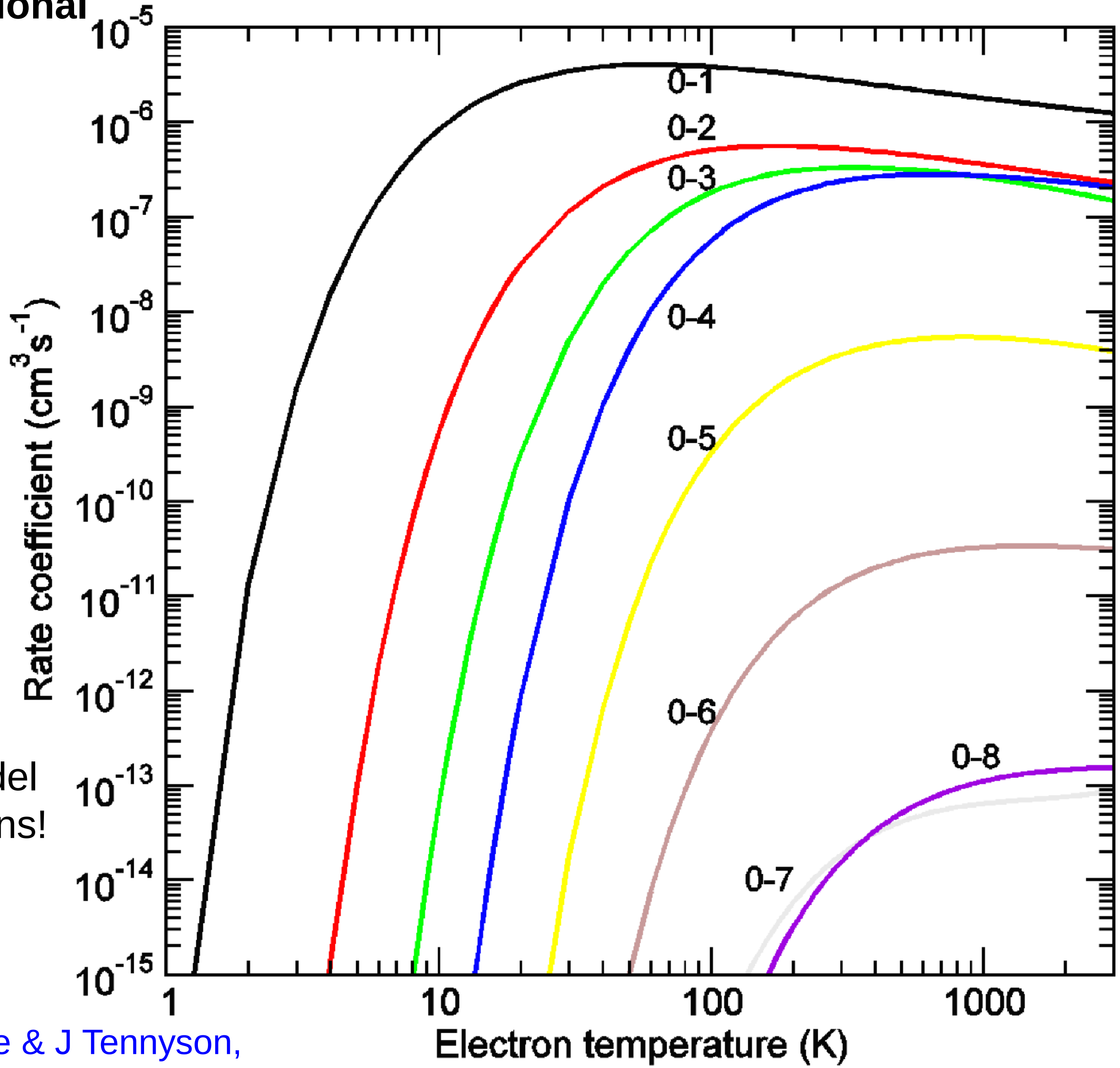


Electron – water (rotationally averaged) elastic cross sections



A Faure, JD Gorfinkel & J Tennyson, *J Phys* B, **37**, 801 (2004)

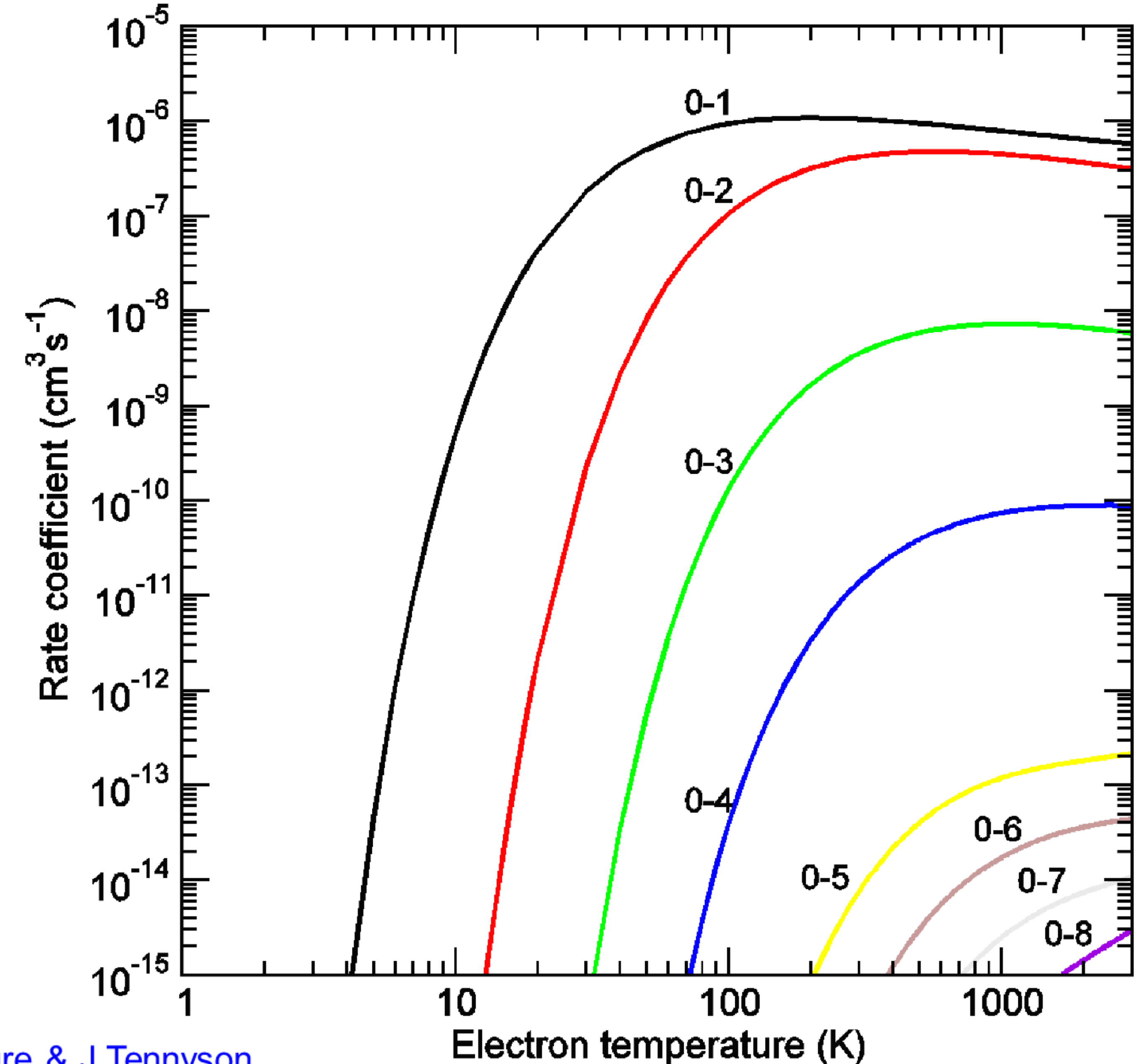
Electron impact rotational excitation of ArH^+
“Argonium”



Barlow et al (2013, Science, 342, 1343) used CH+ rates to model their observed emissions!

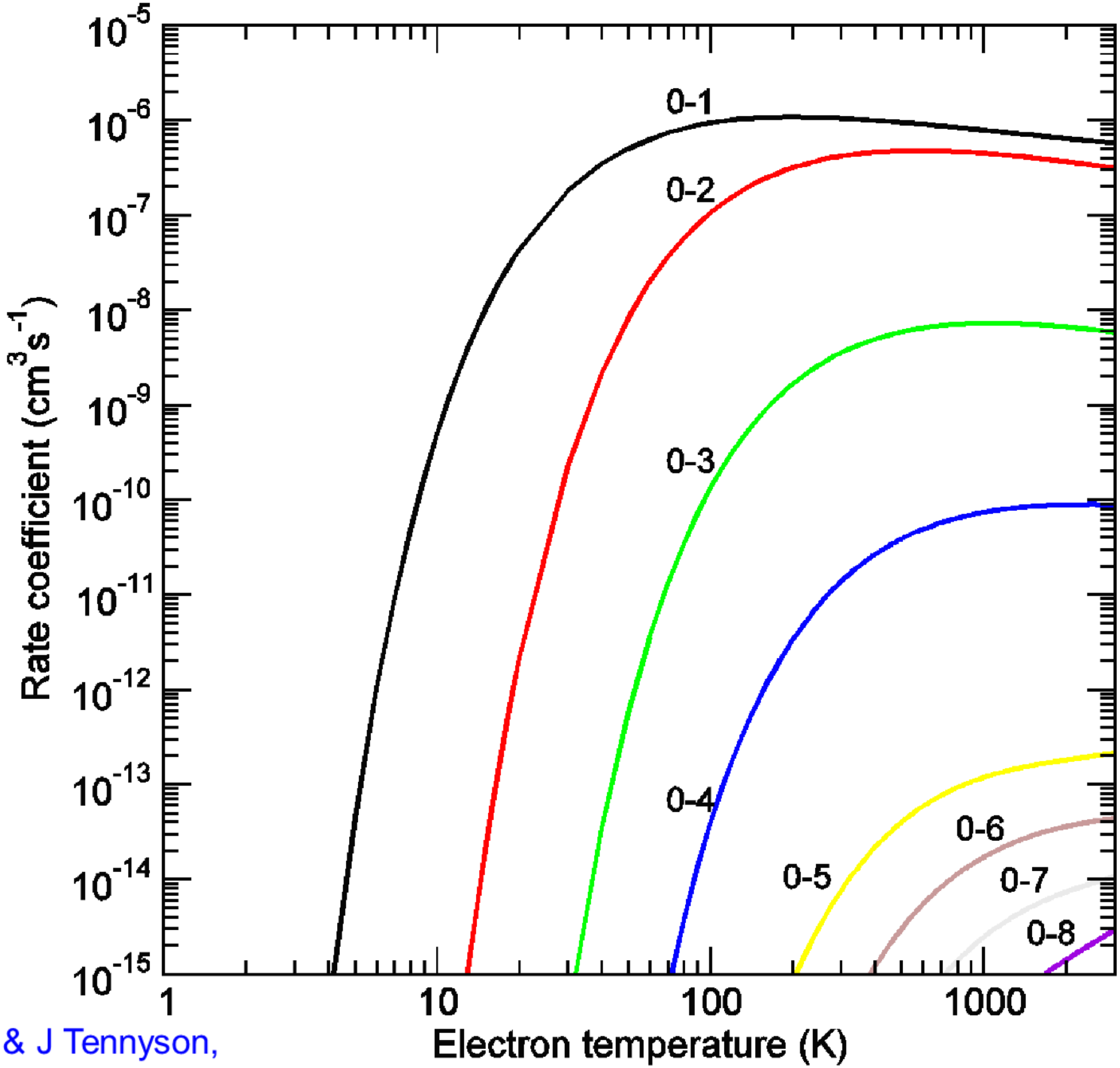
JR Hamilton, A Faure & J Tennyson, 2015, MNRAS, (to be submitted)

Electron impact rotational excitation of CH^+



JR Hamilton, A Faure & J Tennyson, 2015, MNRAS, (to be submitted)

Electron impact rotational excitation of HeH^+



JR Hamilton, A Faure & J Tennyson, 2015, MNRAS, (to be submitted)

Electron impact excitation rates available for:

- Molecular ions:

  Linear: NO^+, ArH^+, CH^+, HeH^+, HCO^+, H_2^+, HD^+

  Symmetric top: H_3^+, H_3O^+

- Neutral species:

  Asymmetric top: H_2O

  Linear: SiO, CS, SIO, HCN, HNC (hyperfine),

  CN (fine structure)

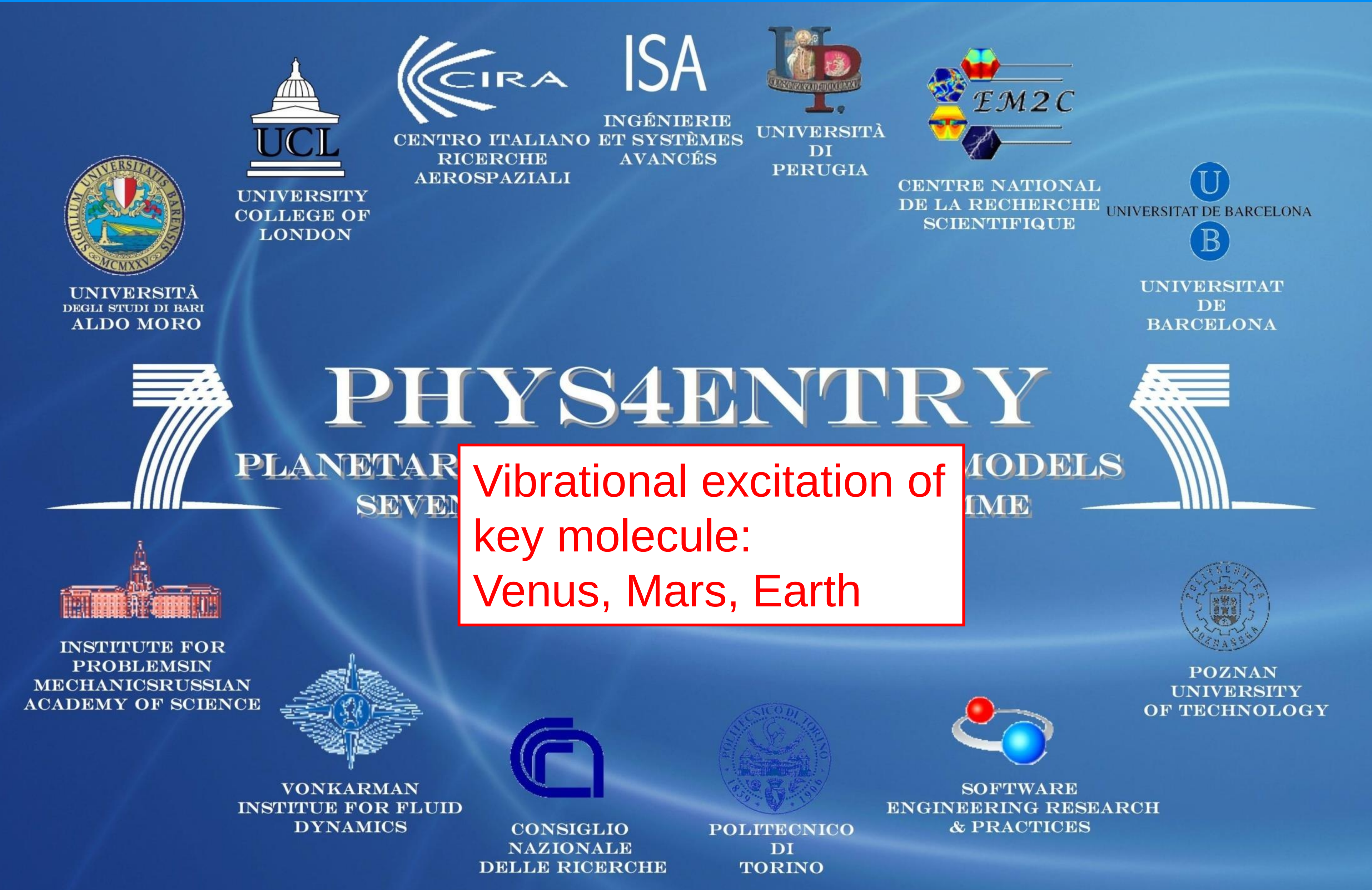
- Planned: OH, OH^+, SH^+

Improved threshold correction

Most data in BASECOL

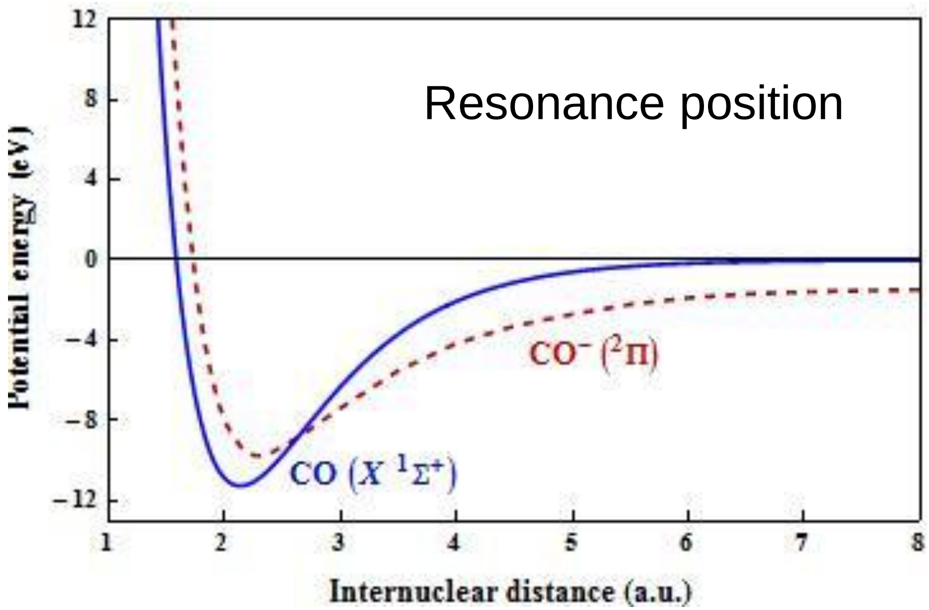
Others? Suggestions?

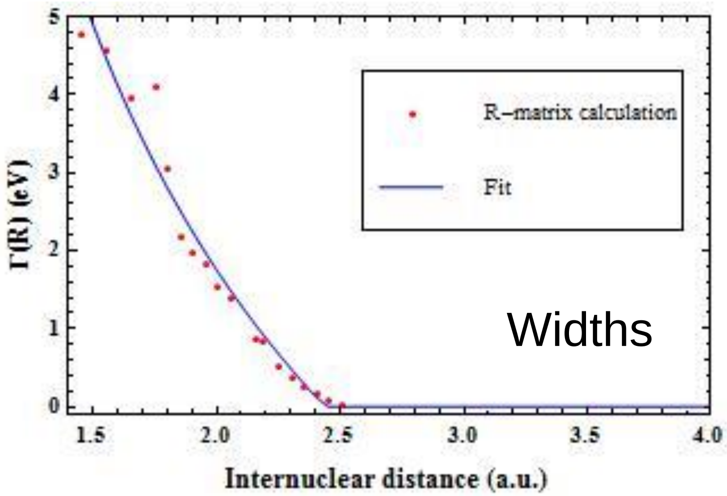
Re-entry physics:
plasmas created on spacecraft (rocket) re-entry



Vibrational excitation of key molecule:
Venus, Mars, Earth

Electron – CO: $^2\Pi$ resonance



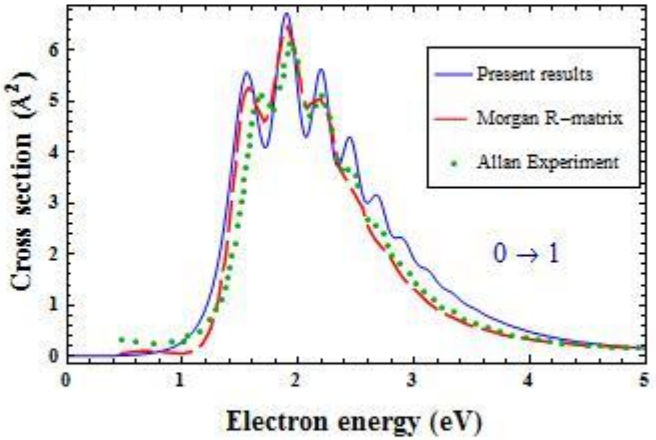


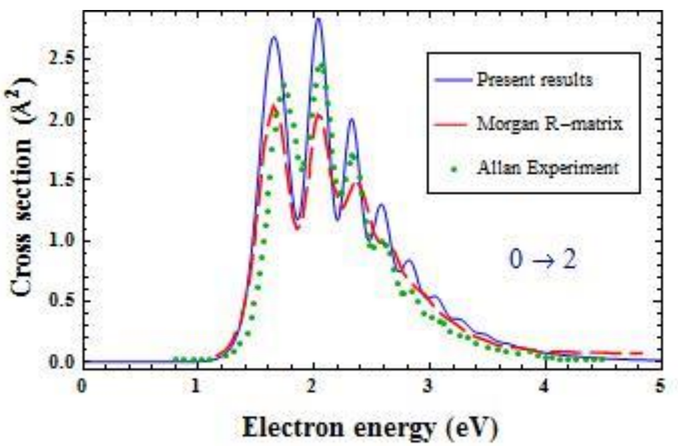
R-matrix resonance positions and widths

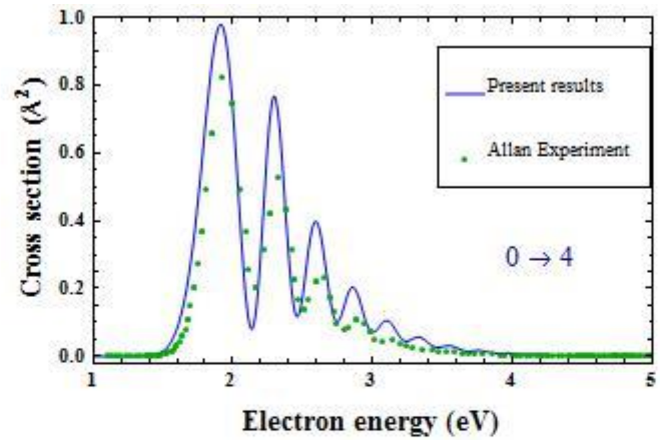
Static exchange plus polarisation (SEP) model

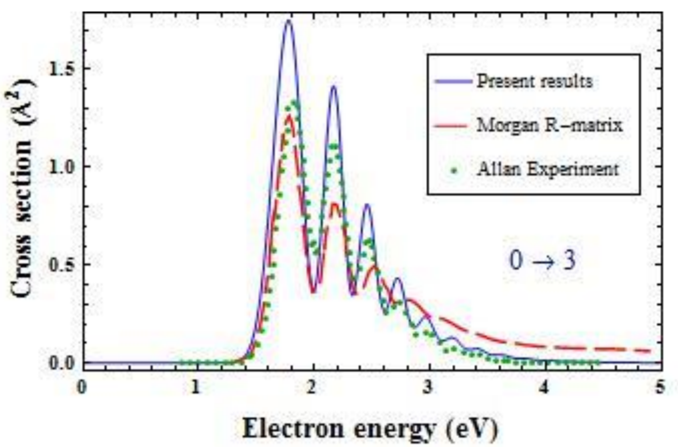
Electron – CO:

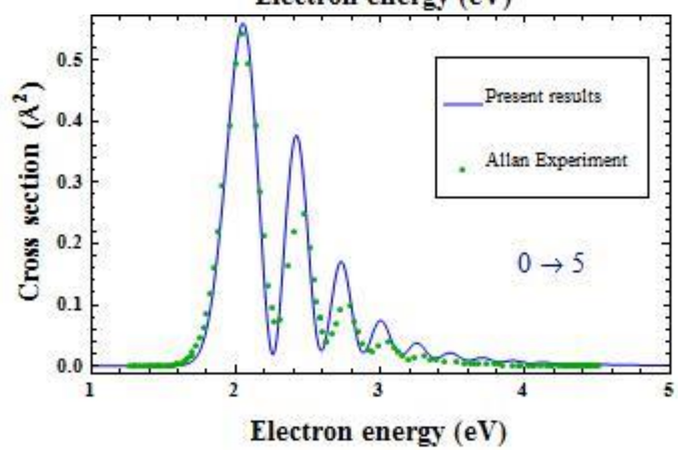
resonance enhanced vibrational excitation 0 → v'







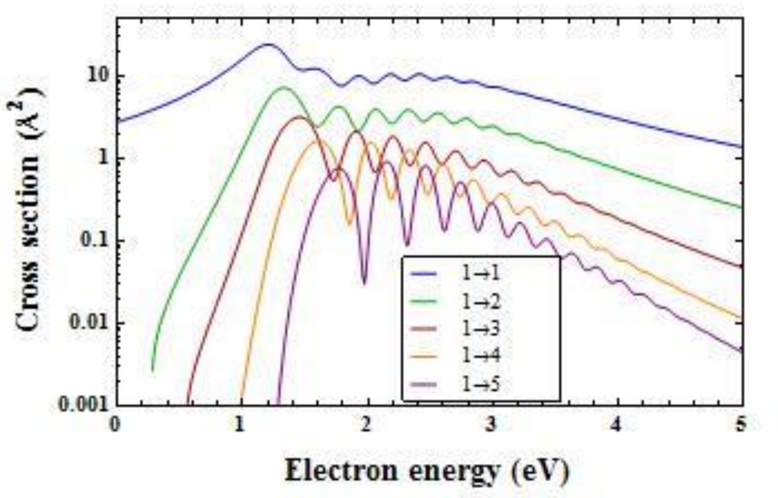


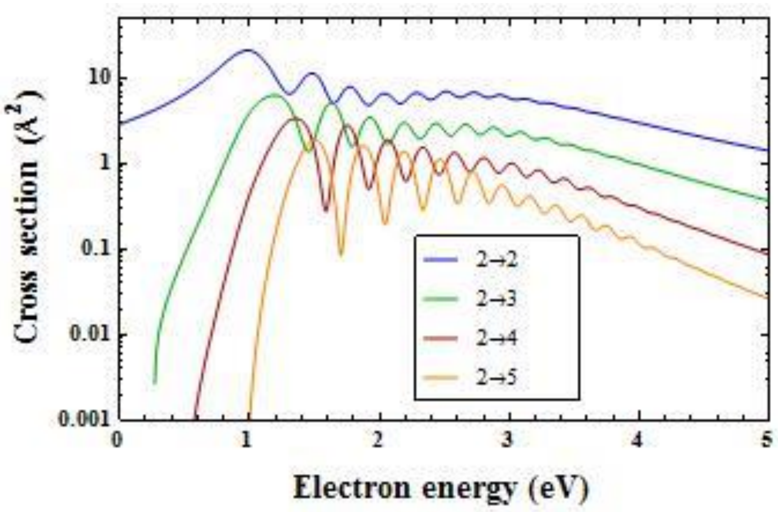


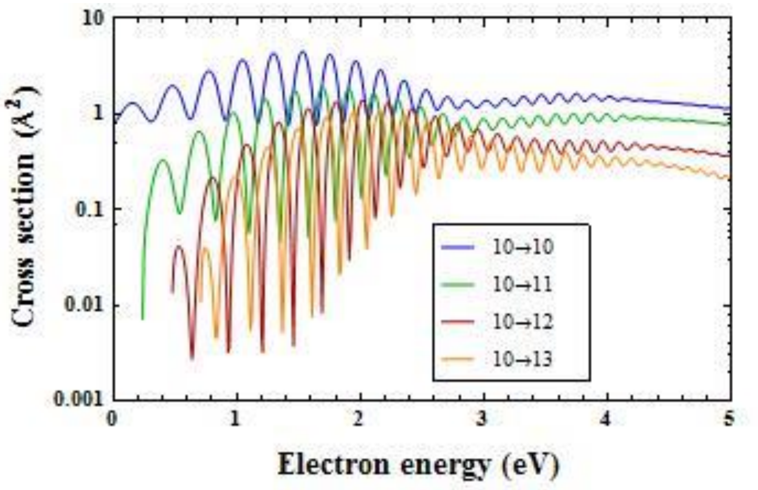
Electron – CO:

resonance enhanced vibrational excitation

High v' – v"(>0)







V Laporte, CM Cassidy, J Tennyson & R Celliberto,
Plasma Sources Science and Technology 21, 045005 (2012)

Calculations extended to:

e + NO(v”) → e + NO(v’)

e + NO(v”) → N + O^-

e + O_2(v”) → e + O_2(v’)

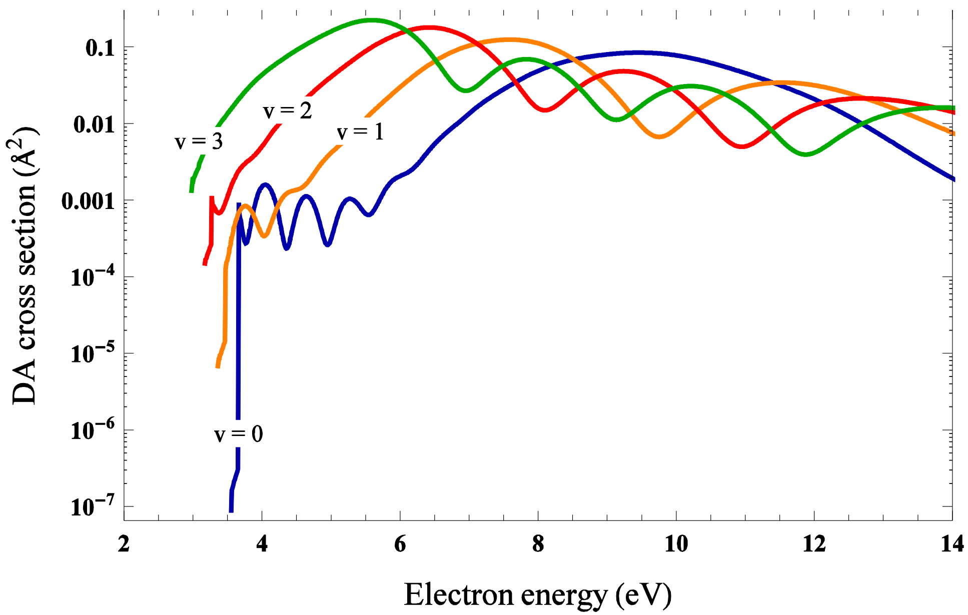
V. Laporta, R. Celiberto & J. Tennyson, Plasma Sources Sci. Technol., 22, 025001 (2013)

e + O_2(v”) → O + O^-

e + N_2(v”) → e + N_2(v’)

V. Laporta, D.A. Little, R. Celiberto & J. Tennyson, Plasma Sources Sci. Technol. 23, 065002 (2014)
G Colonna, V Laporta, R Celiberto, M Capitelli, V Laporta & J. Tennyson Plasma Sources Sci. Technol. 24 (2015) 035004

Dissociative attachment of O_2



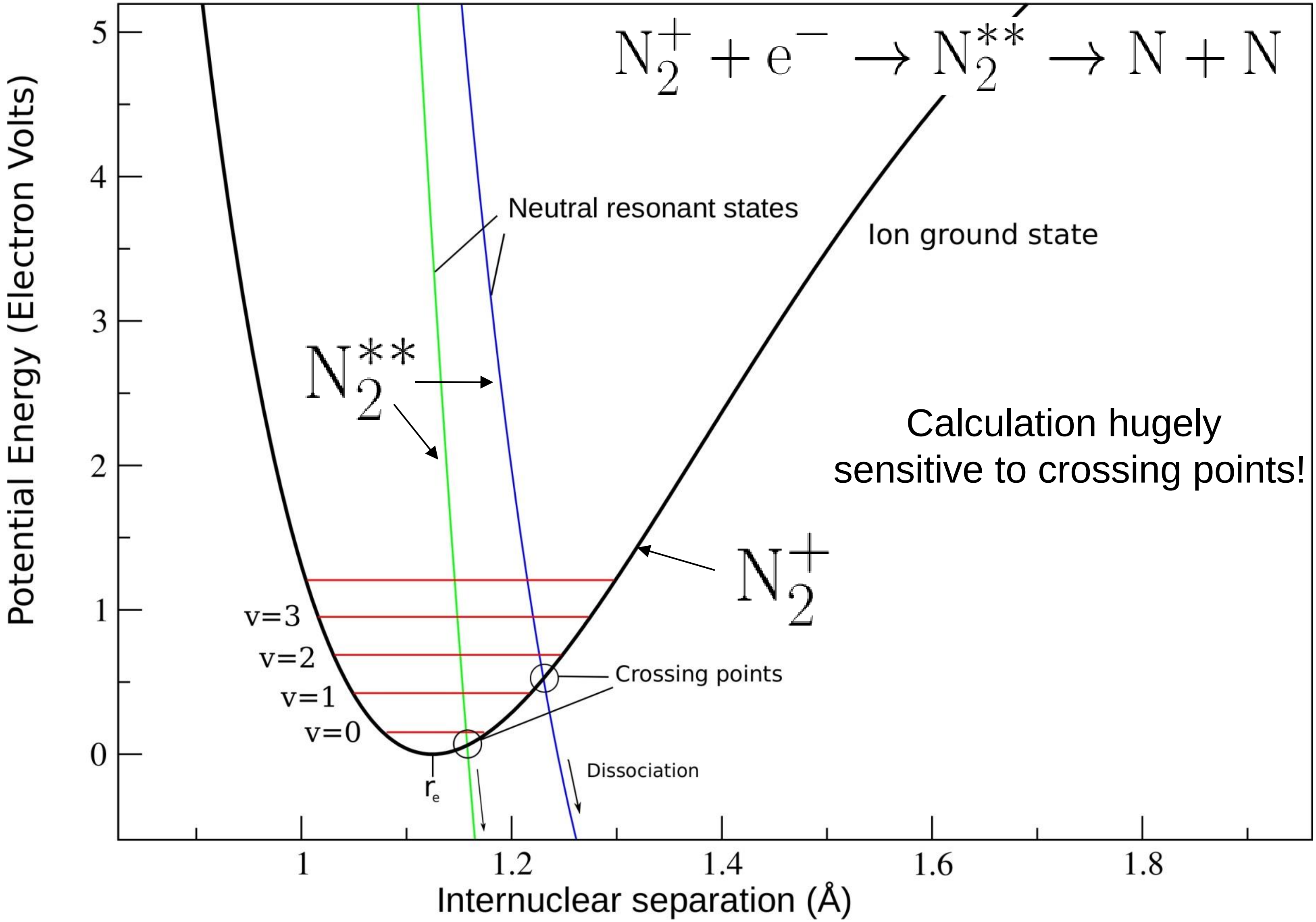
V. Laporta, R. Celiberto & J. Tennyson, Phys. Rev. A, 91, 012701 (2015).

Vincenzo Laporta

Complete data sets for vibrational excitation and dissociative attachment from N_2, O_2, CO, NO

Dissociative recombination (DR)

(Direct process)



Dissociative recombination (DR) and vibrational (+rotational) excitation of molecular ions

(Ioan Schneider, Le Havre)

Recent work:

DR of N_2^+

$$\mathrm{N_2^+ + e^- \rightarrow N_2^{**} \rightarrow N + N}$$

D.A. Little, K. Chakrabarti, J.Z. Mezei, I. F. Schneider & J. Tennyson, Phys. Rev. A., 90, 052705 (2014).

DR and vibrational excitation of CO^+

J Zs Mezei et al Plasma Sources Sci. Technol. 24 035005 (2015)

Others?